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A demonstration that UO_2 is an f-f type Mott-Hubbard insulator

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We have performed x-ray absorption experiments on uranium dioxide (UO_2) at the O 1s, U 4d, and U 4f edges. We have used the U 4d and 4f spectra to sort the energetic positions of the 5f and the 6d states in the unoccupied band unambiguously. This demonstrates conclusively that UO_2 is an f-f Mott-Hubbard insulator, where the electronic repulsion between f electrons is responsible for the insulating state. Calculations performed within the U-corrected local spin density, and generalized gradient approximations, are in good agreement with experimental results. Calculations using reduced matrix density functional theory without parameter adjustment correctly predict an insulating ground state for this highly correlated system.

PACS numbers:

The insulating phase of a Mott-Hubbard insulator is due to correlation effects associated with electron-electron interaction [1]. The properties of these insulators are substantially different from those of ordinary insulators described by noninteracting electrons in conventional band theory. In an ordinary insulator, if an energy corresponding to the band gap is provided, electrons are excited from the valence band to the conduction band and are delocalized, thereby contributing to the electrical conductivity of the material. However, in a Mott-Hubbard insulator of f-f type for example, if an energy corresponding to the band gap is provided, electrons are excited from one localized f state to another. Since the excited state is localized, the electrons do not contribute to the electrical conductivity.

UO_2 is a known Mott-Hubbard insulator [3]. It is an important technological material since it is the principal fuel used in nuclear reactors for electrical power generation and research. In these systems it typically operates under conditions of high temperature and intense radiation [2]. A primary limitation of UO_2 as a fuel is its comparatively poor thermal conductivity [3]. A comprehensive understanding of the fundamental electronic structure of UO_2, which determines, at least in part, this and other relevant properties, is therefore desirable. More generally, precise experimental determination of the electronic structure provides an opportunity to rigorously test first-principles theoretical approaches developed to predict the properties of highly correlated systems.

The electronic structure of UO_2 has been the subject of several experimental and theoretical investigations over the last several decades. It has been studied using x-ray photoemission spectroscopy (XPS) [4, 5], resonant photoemission spectroscopy (RPES) [6], optical absorption spectroscopy [7, 8], inverse photoemission spectroscopy (IPES) [9], bremsstrahlung isochromat spectroscopy (BIS) [4], x-ray absorption spectroscopy (XAS) [10, 11], and also theoretical methods [11–18]. Based on these experimental and theoretical results, much of the electronic structure of UO_2 has been clarified, but there are several important outstanding issues. One concerns the nature of the insulating state. As mentioned above, UO_2 belongs to a class of strongly correlated materials known as the Mott-Hubbard insulators, in which the electronic repulsion is responsible for the insulating state. However, it is not clear whether it is of f-f type or f-d type. Optical measurement [7, 8], BIS [4, 15], and IPES [9] data suggested that UO_2 is f-d type, while O 1s XAS measurement [11] and theoretical calculations suggested that it is f-f type [11, 16–18]. This question is related directly to the nature of the unoccupied state of UO_2. Since the top of the occupied state is dominated by f electrons, UO_2 is an f-f type insulator if the bottom of the unoccupied state is dominated by f character while it is f-d type if the bottom of the unoccupied state is dominated by d character.

In order to address the issue, we have performed XAS measurements not only at the O 1s, but also at the U 4f and U 4d edges. XAS is a powerful method of probing the unoccupied electronic state at a selected site [10, 11]. In the O 1s XAS process, electrons from 1s core level are excited O 2p according to the dipole selection rules. In this case, O 2p is hybridized with U 5f and U 6d in the unoccupied state, and the O 1s XAS spectrum represents the hybridized characters between O 2p and U 5f, and that between O 2p and U 6d. In the case of the U 4f(4d) XAS process, electrons from U 4f(4d) are excited to 6d(5f) in the unoccupied state, respectively. Therefore, comparison between spectra measured at the different edges can provide directly the nature of the unoccupied state. Our data demonstrate experimentally and unambiguously that UO_2 is an f-f type Mott-Hubbard insulator. In parallel, we have performed calculations within

the U-corrected local spin density, and generalized gradient approximations (LSDA+U and GGA+U, respectively). We have also calculated the electronic structure using reduced density matrix functional theory [19, 20] (RDMFT). We compare the results of these calculations with the experimental XAS data.

A depleted $UO_2(100)$ single crystal of $\sim$3 x 3 mm^2 with thickness of $\sim$0.5 mm was prepared from a large crystal. Calculated mass and activity were $\sim$50 mg and $\sim$18.5 nanoCurie, respectively. Sample dimensions were chosen to minimize the activity while being consistent with the beam spot dimensions of $\sim$0.1 x 1 mm^2. XAS measurements performed at Beam Line 8.0.1 [21] of the Advanced Light Source at Lawrence Berkeley National Laboratory. The undulator and spherical grating monochromator provide linear polarized photons with resolving power (E/ΔE) up to 6000. XAS spectra were accumulated by measuring the total fluorescent yield (TFY), which is bulk sensitive compared to the total electron yield (TEY). All XAS spectra were normalized to the beam flux measured by a clean gold mesh. The resolution of the XAS measurement is estimated to be better than 0.3 eV.

The upper part of Fig. 1 shows the XAS spectrum measured at the O 1s edge. The assignments for the peaks are given according to the reference [11]. The 4 peaks measured are assigned as a through d. In order to account for this spectrum, we need to understand the hybridization between O 2p and U 5f(6d) in the unoccupied state. Through the hybridization, O 2p electrons transfer to the unoccupied U 5f(6d) state and there is the possibility that O 1s electrons can be excited to the empty O 2p state in the XAS process governed by the dipole selection rules $\Delta\ell = \pm 1$. Without the hybridization, there would not exist such a structure in O 1s XAS because O 2p^6 is filled completely and cannot accommodate additional electrons.

UO_2 is composed of U^{4+} and O^{2-} and its ground state configuration can be written as U $6p^6 5f^2 6d^0 7s^0$ O $2p^6$ ($5f^2$ configuration) [11]. When hybridization between oxygen and uranium is activated, the $5f^2$ configuration is coupled with $5f^3\underline{L}$ and $5f^2 6d^1\underline{L}$ configurations ($\underline{L}$ denotes a hole in O 2p), where $5f^3\underline{L}$ ($5f^2 6d^1\underline{L}$) denotes the configuration obtained from $5f^2$ by transferring a O 2p electron to the 5f (6d) state. Only one hole in O 2p has been considered, and configurations involving 7s states are neglected. With hybridization, therefore, the ground state becomes a combination of $5f^2$, $5f^3\underline{L}$, and $5f^2 6d^1\underline{L}$ configurations. During the O 1s XAS process, an O 1s electron is excited to the empty O 2p level. This implies that after x-ray absorption, the lowest-energy final states accessible are mixtures of $\underline{c}5f^3$ and $\underline{c}5f^2 6d^1$ configurations ($\underline{c}$ denotes a hole in O 1s). If we neglect the hybridization between 5f-6d as it is expected to be small, one can consider that O 1s XAS will consist of the two types of configurations of $\underline{c}5f^3$ and $\underline{c}5f^2 6d^1$.

The structures a and b in the O 1s XAS shown in Fig. 1 can be attributed to the $\underline{c}5f^3$ configuration [11]. In fact, the first-principles calculations based on the LSDA+U [11] and the hybrid density-functional theory [12], as well as our calculations shown in Fig. 2 (LSDA+U and GGA+U) show that the unoccupied 5f states are lower in energy than the unoccupied 6d states. Furthermore, for the $5f^3$ electronic interactions, both the spin-orbit splitting and the cubic crystal-field splitting are approximately 1 eV [11, 13]. These electronic interactions of the spin-orbit splitting and the cubic crystal-field splitting lead to a very complex multiplet structure that may spread over several eV for $5f^3$ state, producing the structures a and b in the O 1s XAS. Therefore, the structures a and b reflect the $5f^3$ multiplet states hybridized with the O 2p state.

Next we consider the $\underline{c}5f^2 6d^1$ configuration. Under a cubic crystal-field symmetry, 6d states are split into the two fold degenerate e_g and the three fold degenerate t_{2g} states [7, 8]. The e_g states are lower in energy than the t_{2g} states. If we neglect the spin-orbit coupling of 6d states and the 5f-6d interaction, there is no 6d multiplet interaction because there is only one 6d electron. Therefore, the possible configurations are $5f^2 6e_g^1$ and $5f^2 6t_{2g}^1$, which can be attributed to the structures c and d, respectively, in the O 1s XAS shown in Fig. 1. The energy separation between the structures c and d is 4.3 eV, which is in agreement with the 4.4 eV energy splitting between $6d(e_g)$ and $6d(t_{2g})$ in UO_2 found within a multiple scattering approach [22]. Therefore, the structures c and d are attributed to U $6d(e_g)$ and U $6d(t_{2g})$ states split by the cubic crystal-field, hybridized with O 2p state.

Our O 1s XAS spectrum measured in TFY mode from a single crystal UO_2 is in agreement with previous O 1s XAS data measured in TEY mode from polycrystalline UO_2 [11], and confirms that the U 5f state is located lower in energy than the U 6d state in the unoccupied state. Therefore, UO_2 can be classified as an f-f Mott-Hubbard insulator [16]. But it is in disagreement with other findings [4, 9, 15], in which UO_2 is classified as an f-d type insulator based on optical, BIS, and IPES measurements.

So far, we have used only theoretical arguments to analyze the O 1s XAS spectrum, which concludes an f-f type insulating nature of UO_2. Therefore, the conclusion is still ambiguous as the energetic positions of the unoccupied 5f and 6d states could be switched in reality. Is there any way to confirm the f-f nature of UO_2 on the basis of XAS experimental data alone? One way is to excite other core electrons to the unoccupied states of 5f and 6d, e. g., to perform $d \rightarrow 5f$ and $f \rightarrow 6d$ XAS measurements. For the $d \rightarrow 5f$ XAS, in principle, both the core levels U 5d and U 4d can be used. But the spin-orbit interaction of the core level 5d is smaller than the core-valence electrostatic interactions in $5d \rightarrow 5f$ transition, and this effectively smears out the transitions, encapsu-

lating both the $5d_{5/2} \rightarrow 5f$ and $5d_{3/2} \rightarrow 5f$ peaks within the giant resonance, thus making identification of the $5f$ in the unoccupied state [10] difficult. We, therefore, selected the $4d \rightarrow 5f$ transition.

As shown in Fig. 1, the U $4d_{5/2} \rightarrow 5f$ and U $4d_{3/2} \rightarrow 5f$ XAS spectra show features at the energy positions of the structures a and b measured in O $1s$ XAS, while they do not show any features at the energy positions of the structures c and d. This results from the fact that the structures a and b originate from the f character of the unoccupied states. To detect the d character of the unoccupied states, we used the U $4f_{7/2} \rightarrow 6d$ XAS. In this case, U $4f_{7/2} \rightarrow 6d$ XAS spectrum [23] does not show any features at the positions of the structures a and b, but shows features at the positions of structures c and d, which are derived from the d character. Therefore, the combination of the $4d \rightarrow 5f$ and $4f \rightarrow 6d$ XAS measurements, with O $1s$ XAS, as shown in Fig. 1, is conclusive experimental evidence that the $5f$ state is located lower in energy than $6d$ in the unoccupied state of UO_2, and that UO_2 is an f-f Mott-Hubbard insulator. The charge transfer energy, Δ, and the Coulomb repulsion energy, U, are the basic parameters that characterize the Mott-Hubbard ($\Delta > U$) and Charge-Transfer insulators ($\Delta < U$) [1]. For UO_2, $\Delta = 6.5$ eV [11, 16] and U=4.6 eV [4].

The suggestion of an f-d type insulator is mainly based on optical measurement [8] and the interpretation of the BIS data [4]. We first consider the optical measurement. As shown in the upper part of Fig. 2, it is well known from the XPS data of UO_2 [4–6] that the occupied valence band of UO_2 is composed of both the O $2p$ band, which tails off at approximately -4 eV relative to E_F, and the occupied U $5f$ state, which lies at about -1.5 eV relative to E_F. In the optical measurement, the O $2p$ and the U $5f$ electrons are excited to the unoccupied states, obeying the dipole selection rules. Therefore, neither the O $2p$ nor the U $5f$ electrons can access the unoccupied $5f$ state. They can only access the unoccupied $6d$ state. In fact, the first-principles calculations of the electronic structure of UO_2, which include correlation effects [11, 12, 14, 17], and our calculations of LSDA+U and GGA+U shown in Fig. 2 indicate clearly that the unoccupied U $5f$ and U $6d$ states coexist and furthermore, the onset of the two unoccupied states occurs at about the same energy above the band gap, but the density of state of the unoccupied U $5f$ state is several hundred times stronger than that of the U $6d$ state at the position of the onset. The DOS of the U $5f$ state is predominant at the bottom of the unoccupied state and the DOS of the U $6d$ is relatively extremely small, but not zero. This might explain why the f-d type is suggested on the basis of the optical measurement. Secondly, the suggestion of f-d type based on the BIS measurement [4] arose from the interpretation of a shoulder, assigned to the U $6d$ state, at the beginning of the BIS spectrum. However, if we take the fact into account that the cross section for the f state is dominated at the high energy used for BIS measurement (1.5 keV), it is difficult to believe that the shoulder originated from the $6d$ state.

We note that pure UO_2 is known to be a good insulator (conductance at room temperature is approximately 4×10^{-3} $(\Omega\text{cm})^{-1}$) [24] with a band gap of only 2.1 eV [7], which is comparable with other common semiconductors. Therefore, conceptually, the f-f type is preferred over the f-d type to explain the insulating nature of UO_2. If UO_2 had a f-d type band gap, the d state being more delocalized in the conduction band would contribute more to the conductivity than the f state, and UO_2 would be a semiconductor.

As can be seen from Fig. 2, the LSDA+U and GGA+U results agree well not only with the experimental findings, but also with previous calculations [11, 12], and imply that UO_2 is an f-f Mott-Hubbard insulator. The RDMFT result correctly predicts an insulating ground state for this highly correlated system, which is a significant result in light of the fact that the gap is obtained in the absence of any long range spin order (consistent with Mott-type physics). RDMFT also correctly predicts that the lowest unoccupied states have an f-character . However, the predicted band gap (4.3 eV) is large compared to the experimental result (2.1 eV) while the order and intensities of the other states are incorrect. As indicated in the reference [19], this could be due to an incorrect choice for the value of α, which is the adjustable parameter in RDMFT and represents the degree of correlation (for example, α=1 in the uncorrelated limit and α=1/2 in the strongly correlated limit). We used α=0.565, which is a good value for transition metal oxides, but probably not a good value for UO_2. In order to refine the α for UO_2 any further, one could do one of two things: make α a functional of density or fit to best reproduce results for a wide range of materials in actinides [19].

Finally in light of these results, it would be desirable to comprehensively characterize the electronic structure that determines the insulating nature of the higher oxides of uranium. XPS studies indicate that the intensity of the U $5f$ peak located near E_F is decreased as the oxidization increases, and even disappears in UO_3 [5]. Clearly, as the oxidation increases, more electrons are transferred from the U $5f$ to the O $2p$ states.

In conclusion, O $1s$ XAS data demonstrate that O $2p$ and U $5f(6d)$ hybridize in the unoccupied state and produces the complex structure in O $1s$ XAS of UO_2. The hybridization between O $2p$ and U $5f$ is responsible for the structure in the lower energy region and the hybridization between O $2p$ and U $6d$ is responsible for the structure in the higher energy region of the O $1s$ XAS of UO_2. The U $4d \rightarrow 5f$ and U $4f \rightarrow 6d$ XAS provide a conclusive experimental demonstration that the $5f$ state is located lower in energy than $6d$ in the unoccupied state, and that UO_2 is an f-f Mott-Hubbard insulator. This

result is also confirmed by our LSDA+U and GGA+U theoretical calculations.

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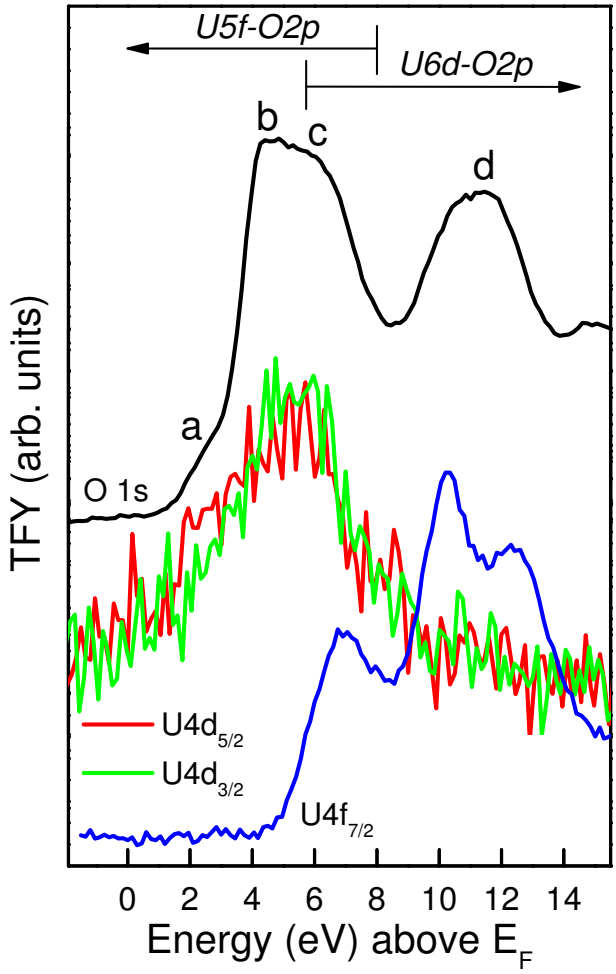

FIG. 1: (Color online) Experimental XAS spectra at the edges of O $1s$, U $4d_{5/2}$, U $4d_{3/2}$, and U $4f_{7/2}$ of a single crystal of UO_2(100). The x-axis is an energy scale and the Fermi energy (E_F) is defined as $E = 0$, which is obtained by subtracting the binding energy of the core level from the calibrated photon energy used for the XAS measurement. All the XAS spectra are measured in the TFY mode. For O $1s$ XAS spectrum, the structures a and b originate from the hybridization between O $2p$ and U $5f$, while the structures c and d originate from that between O $2p$ and U $6d$.

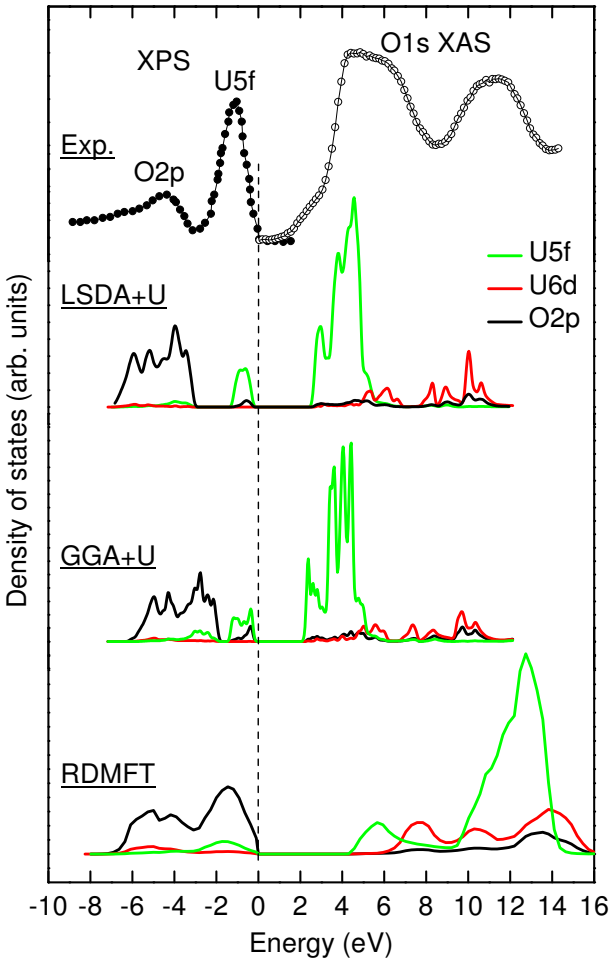

FIG. 2: (Color online) Comparison between experimental data and theoretical calculations. The XPS spectrum is taken from Reference [6] and the O 1s XAS spectrum is that of Fig. 1. For LSDA+U, U=5.04 eV and U=24.10 eV are applied to U 5f and O 2p, respectively. For GGA+U, U=4.49 eV is applied to U 5f. Spin-orbit interaction is included for all three calculations.